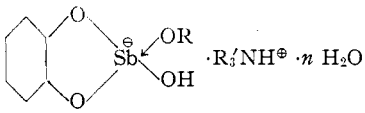
acetone–water mixtures. The properties of the compounds are listed in Table I.

Sodium Antimonyltartratecatechol.—Tartaric acid (16 g.) and sodium bicarbonate (32 g.) were dissolved in 180 ml. of water and heated to 80°. Antimonylcatechol (27.6 g.) was added slowly. After the reaction was completed, the solution was filtered hot and cooled. The product crystallized on standing and was recrystallized from water.

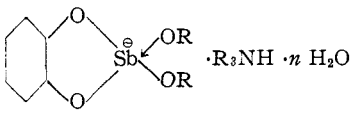
Anal. Found: Sb, 29.91, 29.92.

Discussion of Structure

The structure of antimonyl compounds has not been investigated extensively. Doak[5] has shown that arylstibonic acids and their salts conform to a coördinate ion structure which may be represented as $RSb(OH)_5^- \cdot M^+$ in which antimony exhibits a coördination number of six. Similarly, it was suggested in previous work that some benzenearsonous acids are best represented as $RAs(OH)_3^- \cdot H^+$ where arsenic has a coördination number of four.[6] Triethoxystibine in ethanol forms the ion $(C_2H_5O)_4Sb^-$ which has strong acid properties[1] and the antimony-bis-catecholates have been postulated by Bodendorf[7] to have a coördinate ion



II

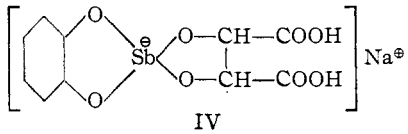


III

(5) G. O. Doak, THIS JOURNAL, **68**, 1991 (1946).
(6) C. K. Banks, *et al.*, *ibid.*, **69**, 5 (1947).
(7) K. Bodendorf, *Pharm. Press.* (Vienna), **38**, 8 (1933).

structure. By analogy, these compounds might have structures II or III.

The strict one-to-one ratio of antimony to nitrogen, the water solubility, ionic type of conductance, all favor such a structural interpretation. Furthermore, the tartaric acid–antimonylcatechol complex (IV), can be explained by a similar postulation.



IV

A comparison of the experimental data with the postulated structures is given in Table II.

While these structures appear to satisfactorily explain the antimonylcatechols and related compounds, all postulations as to the structures of the antimony derivatives of tartaric, citric and malic acids are inadequate to explain the large number of variations obtained. While previous work has suggested that the compounds form complex ions, it is possible that reëxamination of the data in the light of the requirements for coördinate structures may elucidate the nature of the chemical linkages.

Summary

1. Antimonylcatechol was found to react with alcohols and amines to form antimonylcatechol–alcohol–amine complexes having the properties of salts. Fourteen such compounds involving various alcohols and amines are reported.

2. The compounds are best explained as amine salts of an antimonylcatechol coördinate acid.

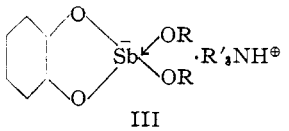
DETROIT, MICHIGAN RECEIVED AUGUST 18, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND CO.]

Antimonylcatechol. II. Coördinates with Aminoalcohols

BY L. M. WHEELER AND C. K. BANKS

In the previous paper of this series[1] it was shown that antimonylcatechol would react with alcohols in the presence of amines to form compounds which could be represented by formula III. It was considered of interest to determine if aminoalcohols would also form similar compounds, and under what specific conditions.



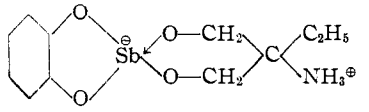
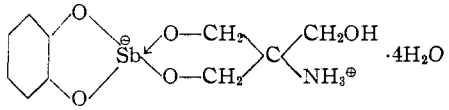
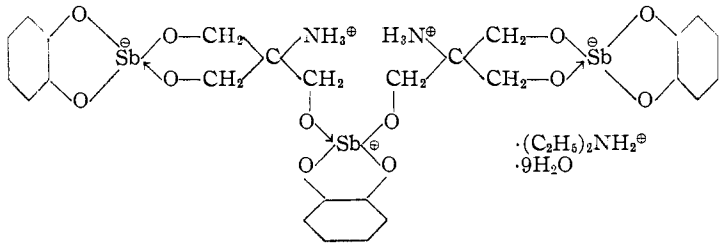
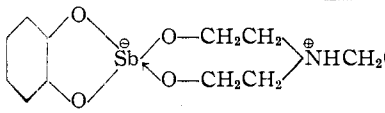
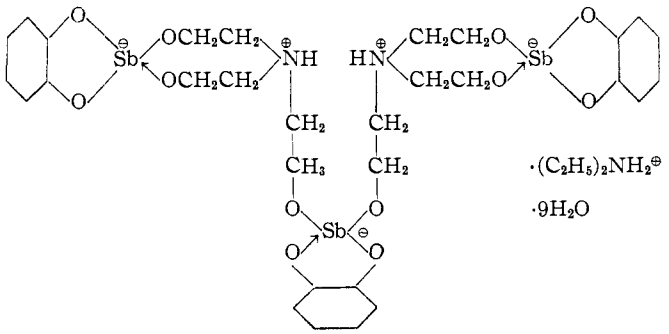
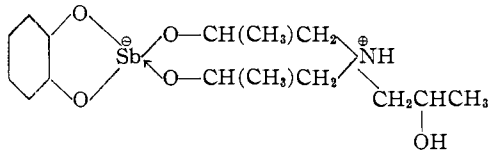
III

Antimonylcatechol was dissolved by aqueous solutions of amino-alcohols when the aminoalcohol was in molecular excess.[2] It was frequently difficult to isolate the products directly from such reaction mixtures. They were easily isolated, however, when antimonylcatechol and the aminoalcohol reacted in aqueous suspension in the presence of an excess of ammonia or diethylamine. The product appeared to be independent of the amine used to catalyze the reaction. When the ratios of reactants were varied, the isolated products were more complex and appeared to incorporate a portion of the catalytic amine.

The products resulting from equimolar reaction were stable as solids and dissolved in water to give solutions which hydrolyzed slowly on standing. An excess of any amine appeared to prevent this hydrolysis. Like the products derived from amines and alcohols, the compounds appeared to have the properties of salts. When two moles of antimonylcatechol reacted with one of a poly-

(1) Wheeler and Banks, THIS JOURNAL, **70**, 1264 (1948).
(2) J. G. Feinberg, U. S. Patent 2,330,962, Oct., 1943.

TABLE I

Reactants—moles Antimonylcatechol	Reactants—moles Aminoalcohol	Postulated structure	M. p., °C.	Assays—% Antimony Calcd.	Antimony Found	Nitrogen Calcd.	Nitrogen Found
1	1		114–115	28.99	28.95	3.33	3.45
1	1		110	28.85	28.74	3.31	3.33
2	1		174–176	31.37	31.25	3.61	3.60
1	1		258–260	29.41	29.43	3.38	3.52
2	1		107	29.91	29.80	3.44	3.48
1	1		114	28.98	28.97	3.33	3.36

hydric aminoalcohol in the presence of another amine, the products were less stable, tending to decompose in solid form. Solutions of these compounds had the same properties as before. The condensation products and their postulated structures are listed in Table I.

Experimental

Equimolar Compounds.—Antimonylcatechol (0.1 mole) was suspended in 100 ml. of water containing the aminoalcohol (0.1 mole) and 0.5 mole of ammonia or diethylamine. The temperature was raised to 80° while stirring. As soon as the reaction was complete, the solution was filtered and chilled. The products crystallized on standing and were recrystallized from acetone–water mixtures.

Antimonylcatechol (2): Aminoalcohol (1).—Antimonylcatechol (0.2 mole) and the aminoalcohol (0.1 mole) reacted in 100 ml. of water and 0.5 mole of diethylamine as before. The products were recrystallized from water or acetone–water mixtures.

Summary

Six coördinate complexes of antimonylcatechol with amino-alcohols have been described as to preparation, properties and possible structure.

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